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An open sorption heat storage concept and materials for building heat supply

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Abstract

The potential of an open sorption storage process for space heating and hot water was evaluated using sorptive material namely zeolite 4A (low grade) and salt-based composite. Sorptive material beds of about 55 kg to 74 kg were able to generate an adsorption heat between 3 and 5 kWh and temperature shifts of the process air between 20 K and 25 K depending on the material type, the inlet air water content, and the state of dehydration of the storage materials. The evaluation of the composite material based on $LiCl/MgSO_4$ and $MgCl_2/MgSO_4$ impregnated clinoptilolite (using max. desorption temperature of 110°C) in a rotating heat drum showed that not agglomeration due to sticking of the grains happens, good controllability of the process was possible, and sufficient high temperature shifts for room heating applications were achieved.

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Keywords: Adsorption heat; Open-sorption process; Zeolite; Rotating drum reactor; Renewable heat; Seasonal storage

1. Introduction

Sorption heat stores, which utilize adsorption heat released during hydration processes, have got the potential to be realized as loss free seasonal heat storages to supply hot water and heating energy for households. The possibility to store solar energy in summer und use thermal energy in winter is a key technology to reach high solar fractions in heat supply of domestic buildings compared to conventional solar thermal applications. Recent studies [1-4] have examined the possibilities and restrictions of such storage concepts using synthetic zeolites. Further development

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seems necessary since zeolites need high desorption temperatures quite above the temperatures provided by conventional solar thermal collectors. Also, the cost for synthetic zeolite material has not reached a competitive level for such applications, compared to conventional heating systems based on heat pumps or burning biomass yet. Much additional efforts are made to improve the systems and to utilize new and more economic storage materials.

Beside the mentioned molecular sieves (namely zeolite) also other classes of solids are able to generate heat while being hydrated. Salts and salt-hydrates for example, incorporate water molecules into their lattice-structure and the process is associated with the release of a certain amount of energy in particular the condensation enthalpy of the absorbed water and bond-dissociation enthalpy (similar to sorptive processes). According to literature [5], the amount of enthalpy released during the formation of high hydrate steps out of anhydrate is 2…3 times higher than that of sorptive materials. The amount of water absorbed can reach 100% and more of the weight of some anhydrate salts.

Material properties largely vary during de- and rehydration of salts. Beside the variation of physical properties the most important changes are associated with the metastable transition stages during the formation of hydrate states. The kinetics of the hydration process is mostly affecting the rate of enthalpy release (thermal power) and thus the temperature level in the reactor vessel. Hydration processes of salts are connected with the formation of a layer of liquid solution at the surface of salt grains, possible formation of stable hydrate shells hindering further hydration of the inner parts, formation of cracks and consequently salt-powder due to volume changes and hydrolysis of chloride salts during de-hydrating are some worth mentioning. If impregnated into porous structures hydration behaviour of salt is combined with the sorption properties of a conventional adsorbent. Therefore the slower sorption behavior of salts could eventually be compensated.

In the present project a new process concept has been developed for utilization of salt based sorption materials. An open-sorption drum-reactor was used for characterization of several sorption materials. Details of the working principle and basic measurements have already been published [1]. In contrast to fixed bed reactions a moved bed can avoid over-hydration near the air entrance area and control of reaction is easy and swift compared to large vessel-reactors.

2. Material and Method

Different composite materials were prepared by wet impregnation of the natural zeolite clinoptilolite with solutions of varying salt mixtures. Clinoptilolite was obtained from IPUS GmbH, Rottenmann, Austria and had the following chemical composition except water [%]: SiO_2 70; Al_2O_3 13; Fe_2O_3 1.3; Exchangeable cations [%]: Mg 0.8; K 2.1; Ca 1.7; Na 1.1; removable water at 130°C: H_2O 4.09%. XRD analysis showed the following mineralogical composition [%]: clinoptilolite 81; cristobalite 5-8; mica 2-4; feldspat 4-7. The impregnation method included wetting of the clinoptilolite by an aqueous mineral salt solution at 85°C for two hours, followed by drying at 130°C for 16 hours. The amount and concentration of the wetting solution was calculated to obtain the desired loading of the mineral after drying. Two series of composite materials were prepared, both with particle sizes 0.5 – 1 mm. In series A, the salt loading reached (on a dry weight basis at 150°C) 1.5% LiCl and 13.5% $MgSO_4$ (Cpt-A1); 4.5% LiCl and 10.5% $MgSO_4$ (Cpt-A2); 7.5% LiCl and 7.5% $MgSO_4$ (Cpt-A3). In series B, the salt loading yielded 7.5% $MgSO_4$ and 7.5% $MgCl_2$ (Cpt-B1); 11% $MgSO_4$ and 11% $MgCl_2$ (Cpt-B2).

Dehydration of clinoptilolite occurs until temperatures of 700 – 800°C, depending on Si/Al ratio and exchangeable cations. Since the “tightly bound zeolite water” is required for stabilization of the crystal structure, only the external and the “loosely bound zeolite water” can be removed from the mineral without partial loss of rehydration capacity [6]. Reversible dehydration occurs at heating up to 400 – 550°C [7], whereas higher temperatures cause collapses of the pore structure.

Adsorption measurements were carried out by exposure of 5 g of test material in a layer of about 5 mm depth in an incubation chamber at constant RH of 95% at 22°C, equipped with a precision balance Sartorius AX124 time-dependent mass increase during adsorption of water vapor by the test material was recorded. The results of these measurements lead to the selection of two composites to be tested in the rotating drum reactor. The two materials selected were composites containing 7.5% LiCl and 7.5% $MgSO_4$ (Cpt-A3) and 7.5% $MgSO_4$ and 7.5% $MgCl_2$ (Cpt-B1). The first was selected because of its favorable water uptake capacity the latter because of the more

economic raw-materials. In addition the second composite was impregnated into a material with larger medium grain size in order to reduce pressure drop of the flowing air stream.

Both composites were tested in the rotating drum reactor. Details of the experimental procedure were already published [1]. For comparison measurements of a synthetic zeolite type 4A are included in this study. This type and grade of the used zeolite has comparable costs compared to the composite containing LiCl (Cpt-A3).

3. Results and Discussion

3.1. Results of the water uptake experiments

Moisture adsorption on natural clinoptilolite with different grain sizes are shown in Fig 1.
The measurements were performed at 23°C and 95% RH and show only little dependence of moisture uptake on particle sizes. In the first hour about 63 – 68% of full capacity has been adsorbed on the material.

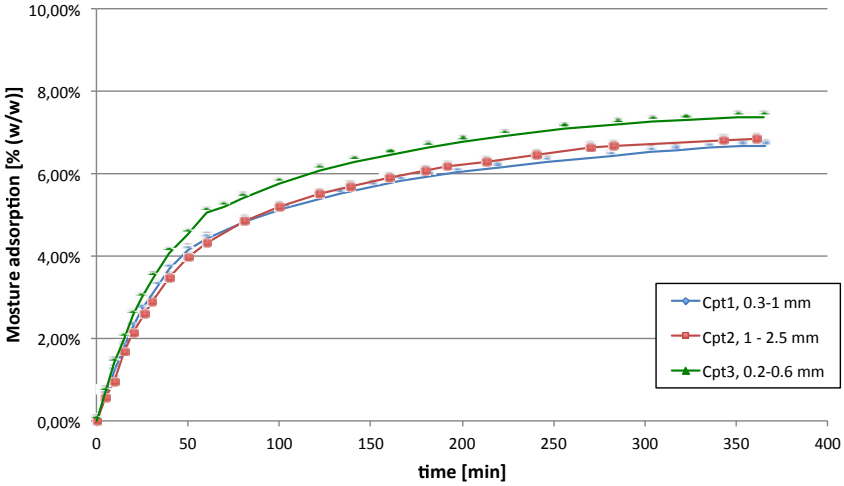


Fig. 1. Moisture adsorption on natural clinoptilolite with different particle sizes.

In contrast to untreated clinoptilolite, the composite materials required longer time to reach full adsorption capacity. After one hour exposure to humidity of series A composites only 32 – 38% of the capacities at 6 hours have been adsorbed (Fig. 2). In series B, the uptake after one hour reached 43% (Cpt-B1) and 37% (Cpt-B2), see Fig. 3.

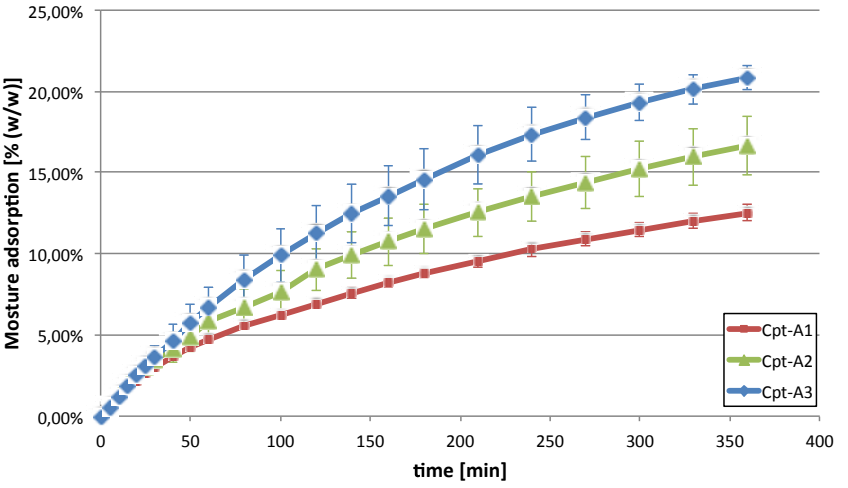


Fig. 2.Series A- Time-dependent moisture adsorption in Cpt – LiCl – MgSO4 – composites.

As a result of the impregnation, the total moisture adsorption capacities increased and have more than doubled. Series B composites are located between Cpt-A1 and Cpt-A2 and are therefore advantageous compared to low LiCl-doping regarding their low material costs. Composites of more than 4.5% LiCl show higher water vapor uptake capacity, up to three times the value of natural clinoptilolite (Cpt-A3, Fig. 2).

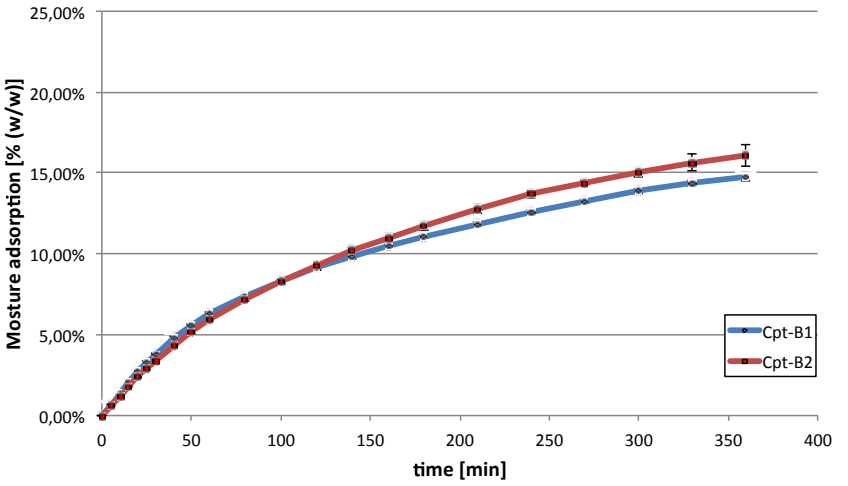


Fig. 3.Series B- Time-dependent moisture adsorption in Cpt – MgCl – MgSO4 – composites.

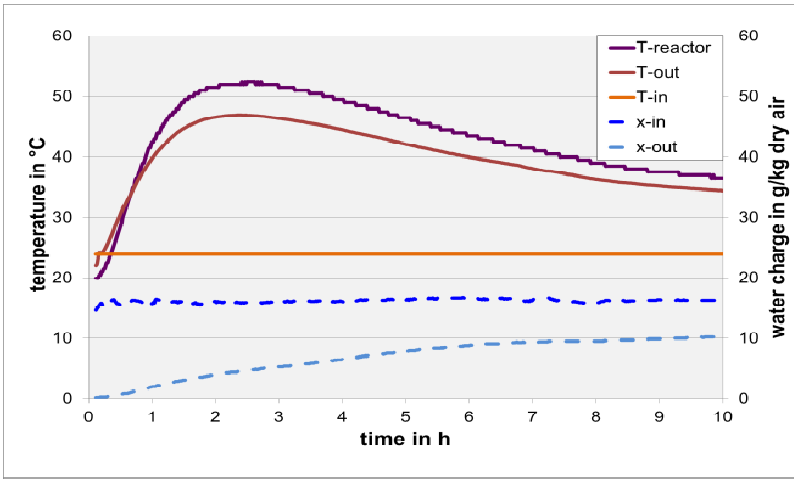
3.2. Evaluation in the revolving drum reactor

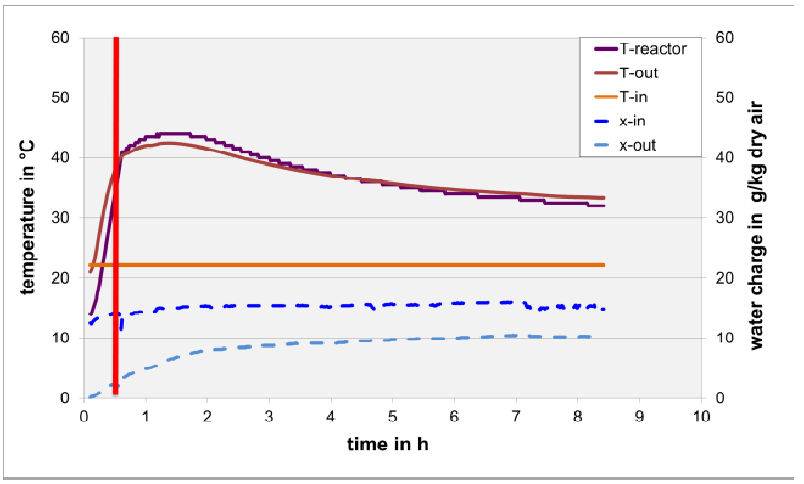
The revolving heat drum reactor is a concept designed for the purpose of heat generation using salt impregnated sorbents. Due to the continuous moved material bed, over-hydration at the site of moisture entrance can be avoided. Since the formation of a reaction front is disabled the maximum temperatures are lower compared to fixed bed reactors. Nevertheless the results found in the experiments are promising since the temperature shifts are high enough for the aim of room heating applications.

In Table 1 the basic parameters of the drum experiments like mass of the filled storage material, desorption temperature, total time of deposition of the batch in a drying oven prior to the drum reactor experiment, water capacity x of the inlet air, air flow rate, and duration of the experiment are listed. The two composite materials are named as Cpt-A3 (composites containing 7.5% LiCl and 7.5% $MgSO_4$), two runs (a) and (b) and Cpt-B1 (composites containing 7.5% $MgSO_4$ and 7.5% $MgCl_2$).

Table 1. Parameters of the heat drum experiments

batch material	mass [kg]	T-des [°C]	t-des [h]	x-in [g/kg dry air]	air flow in [m^3/h]	Duration [h]
Cpt-A3 (a)	68.44	90	72	15.4	63.72	8.05
Cpt-A3 (b)	67.75	90	72	16.19	60.33	10.83
Cpt-B1	74.01	110	72	15.1	69.5	8.43
4A	56.7	230	72	10.5	113.8	5.5





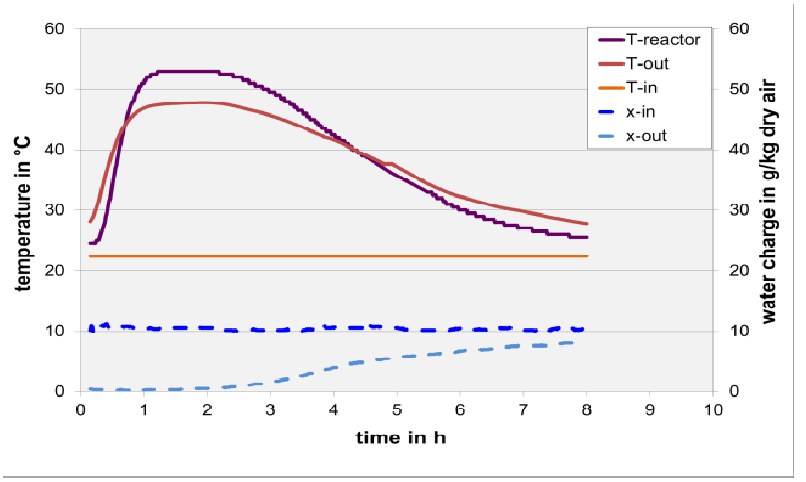
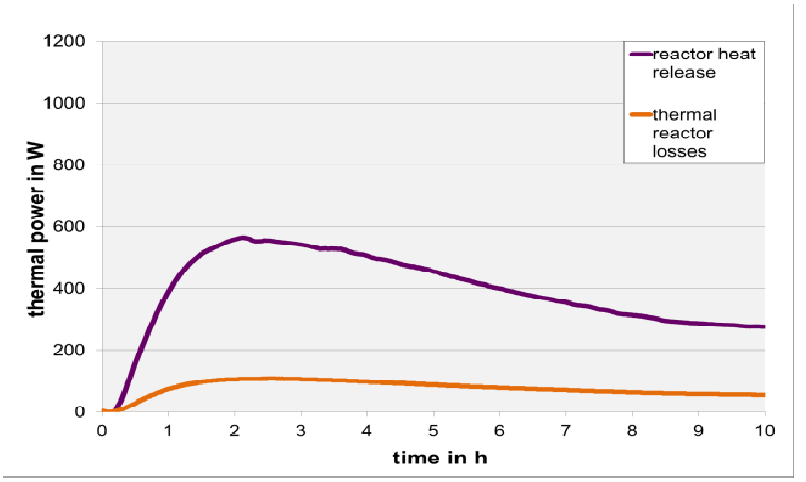


Fig.4. Temperature and moisture measurement of the composite Cpt-A3 (upper diagram). composite Cpt-B1 (middle diagram). and synthetic zeolite 4A (lower diagram)

The results of the measurements are illustrates in the next figure (Fig. 4). Two runs with composite containing LiCl one run with composite containing MgCl2. and a batch of synthetic zeolite are compared. The full lines represent the measured temperatures while the dashed lines indicate the water capacity of the inlet and outlet air.

The red line in one of the experiments shown in Fig. 4 and Fig. 5 indicate a change of the air flow rate. The flow rate at the start of the measurement was approx. twice as high and was reduced due to technical reasons to the value indicated in Table 1. The thermal power of the released heat is indicated in Fig. 5. consisting of heat transferred by the air flow and additional thermal losses of the reactor body (shown as separate curve).



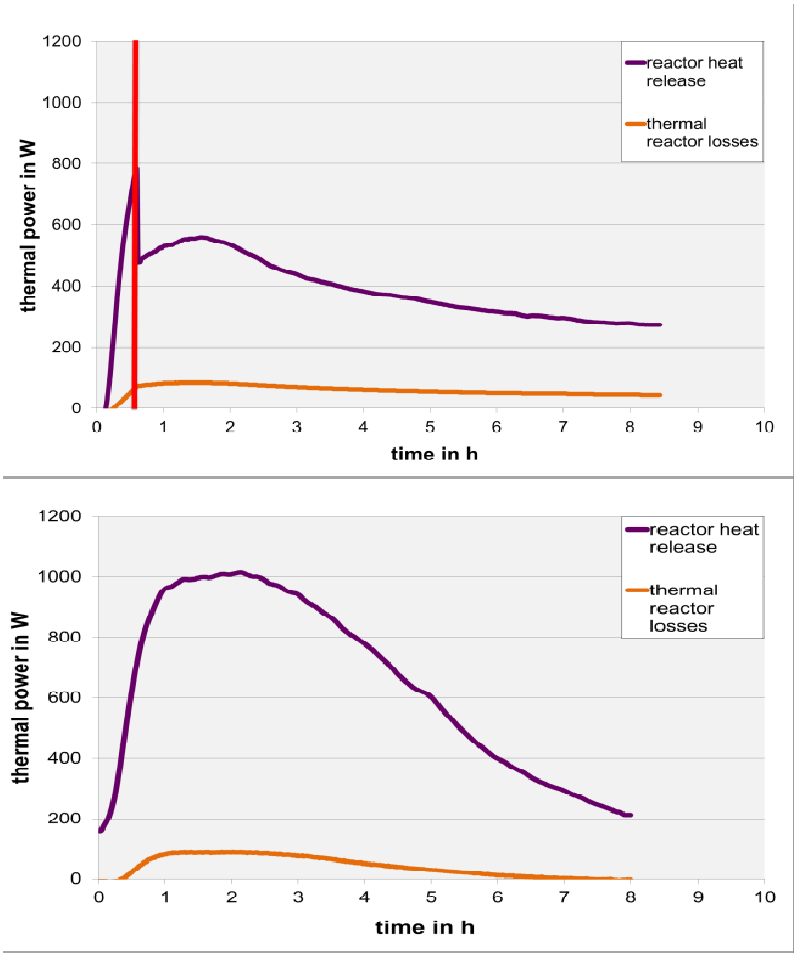


Fig.5. Calculated heat release rate (thermal power) of the composite Cpt-A3 (upper diagram). composite Cpt-B1 (middle diagram).and synthetic zeolite 4A (lower diagram).

It is quite interesting to see. that the composite Cpt-B1 which was selected for economic reasons was able to produce comparable thermal power than Cpt-A3. Other aspects of performance like vapor uptake and reactor temperature was more efficient for the Composite containing LiCl. In Table 2 same representative results like maximum temperature shift, the total water content increase of the storage material, the mass of the involved water, and the total amount of released heat is given.

Table 2. Results of the heat drum experiments

Batch material	ΔT-max [K]	water uptake [%]	water uptake [kg]	Heat release [kWh]
Cpt-A3 (a)	21.8	6.7	4.95	3.32
Cpt-A3 (b)	23.1	8.4	6.2	4.14
Cpt-B1	20.3	5.6	4.41	3.24
4A	25.4	10.0	6.65	5.18

It is worth mentioning that the numbers given in Table 2 are not only material properties but process parameters that result from the kind of material used, the desorption conditions, and the adsorption conditions (air flow rate and humidity. for example). Consequently there is room for further improvement not only by changing material properties but also by varying the experimental setup. For example the batch duration could be extended and therefore additional heat of hydration and sensible heat (due to reactor cool-down) would be available.

4. Conclusions

The measurement of thermochemical storage material based on the salt impregnated clinoptilolite (with maximum desorption temperature of 110°C) in a rotating heat drum showed:

- not agglomeration due to sticking of the grains
- good controllability of the process
- sufficient high temperature shifts for room heating applications
- maximum reactor temperatures in the range of 50°C
- up to 5kWh of released heat for one batch (approx. 70kg)

5. Acknowlegement

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